EFFECT OF COBALT CARBOXYLATE ON THERMAL DEGRADATION OF POLYETHYLENE (HDPE)

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ABSTRACT

This study reports the effect of cobalt carboxylate on thermal degradation of polyethylene (HDPE). The purpose of this study is to gain knowledge and understand behaviour of HDPE film after adding cobalt carboxylate as additive after and before expose to the heating in the oven at 60^0C and also to investigate characteristics of cobalt carboxylate itself. The additives used were three cobalt carboxylate which are cobalt stearate, cobalt palmitate, and cobalt laurate and thin film HDPE containing these additives were prepared with different concentration (0.2% w/w, 0.5% w/w, and 1.0% w/w) by sheeting process. Seventy micron film of HDPE containing different concentration of additives and 3 types of cobalt carboxylate were subsequently exposed to heat and were observed. The characteristics of cobalt carboxylate were monitor by measuring the temperature degradation using TGA (Thermal Gravimetric Analyzer) and to measuring melting point using DSC (Different Scanning Calorimeter). While, the degradation was monitored by measuring the elongation break using tensile machine, changes of structure peak using FTIR and surface film using SEM. In DSC and TGA result, found that, cobalt stearate has high temperature of degradation and high melting point at 121.97^0C; 309.8^0C followed by cobalt palmitate and cobalt laurate at 84.06^0C; 282.74^0C and 69.04^0C; 182.97^0C, respectively. While for FTIR result, Carbonyl Index (CI), which in turn leads to an increase according to the increase of concentration of additives especially cobalt stearate and for tensile test, the percent of break strain decreased inversely proportional with increasing concentration additive present. Results on mechanical properties reveal that samples containing cobalt carboxylate, become mechanically fragile, embrittlement and flaking occurred for samples exposed to longer time periods in the oven for 480 hours. The effect of cobalt carboxylate on air oven aging, show that different behaviour of HDPE at different concentrations will increase proportionally with increasing chain length and follows order $CoSt_3$>$CoPal_3$>$CoLau_3$

ABSTRAK

Kajian ini melaporkan kesan kobat karbosilet terhadap perbuatan merendahkan terma plastik (HDPE). Tujuan kajian untuk mendapatkan pengetahuan dan memahami tabiat HDPE filem selepas menambahkan kobat karbosilet sebagai aditif selepas dan sebelum mendedahkannya kepada pemanasan oven yang bersuhu 60^0C dan juga untuk menyiasat sifat kobat karbosilet itu sendiri. Aditif ini menggunakan tiga kobat karbosilet iaitu kobat stearet, kobat palmitet, dan kobat lauret dan HDPE filem yang mengandungi aditif ini disediakan dengan berlainan kepekatan ((0.2% w/w, 0.5% w/w, and 1.0% w/w) melalui proses kepingan.Tujuh puluh mikron filem HDPE yang mengandungi aditif yang berbeza kepekatan dan 3 jenis kobat karbosilet berikutnya didedahkan kepada haba dan diperhatikan.Sifat kobat karbosilet dilihat dengan mengukur suhu pada perbuatan merendahkan menggunakan TGA dan mengukur takat kecairan menggunakan DSC. Sementara itu, perbuatan merendahkan diperhatikan dengan mengukur kepanjangan putus menggunakan alat mesin ketegangan, perubahan struktur pada kemuncak menggunakan FTIR, dan permukaan filem menggunakan SEM. Di dalam keputusan DSC dan TGA dijumpai, kobat stearet mempunyai suhu yang tinggi pada perbuatan merendahkan dan suhu takat kecairan pada 121.97^0C; 309.8^0C diikuti kobat palmitet dan kobalt lauret masing-masing pada 84.06^0C;282.74^0C and 69.04^0C;182.97^0C. Sementara itu, keputusan FTIR, bagi Indeks karbosil, meningkat berdasarkan peningkatan kepekatan aditif terutamanya kobat stearet dan untuk ujian ketegangan,peratusan putus ketegangan berkurang berkadar songsang dengan peningkatan kepekatan aditif yang hadir. Kajian pada sifat mekanikal mendedahkan, sampel yang mengandungi cobat karbosilet, menjadi rapuh secara mekanik dan mengelupas apabila sampel didedahkan terlalu lama di dalam oven untuk 480 jam. Kesan cobalt carboxylate di dalam oven terlalu lama, menunjukkan HDPE yang berbeza kepekatan aditif akan berkadar langsung dengan meningkatnya pemanjangan rantaian dan diikuti urutan $CoSt_3$>$CoPal_3$>$CoLau_3$.

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LIST OF ABBREVIATIONS

HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
SEM	Scanning Electron Microscopic
DSC	Different Scanning Calorimeter
TGA	Thermogravimetric Analyzer
FTIR	Fourier Transform Infrared Spectroscopy
CS	Cobalt stearate
CP	Cobalt palmitate
CL	Cobalt laurate
V	Volume
MW	Molecular Weight
W	Weight
Co	Cobalt
Mn	Manganese
Fe	Ferum
EAA	Ethylene Acrylic Acid Copolymer
PE	Polyethylene

PP	Polypropylene
DEET	diethyltoluamide
Cl	Carbonyl Index
OPE	Oxidized polyethylene
UV	Ultraviolet
ABS	Acrylonitrile butadiene styrene
DTG	Derivative thermogravimetry
PEO	Polyethylene Oxide
MT	Metric Tonne

LIST OF SYMBOL

$P(x')$	Molecular weight
k_d	Degradation coefficient
M_n	Number average molecular weight
$P^{\bullet}$.	formation
α	alfa
tf	time (days)
T	Temperature (^{0}C)
A	Area (cm)
%	Percentage

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CHAPTER 1

INTRODUCTION

1.1 Background of study

1.1.1 Polyethylene

Polyethylene has achieved a dominant position as a packaging material because of its relatively low cost, versatile properties including high tensile strength, elongation at break, good barrier properties against water borne organisms, lower cost, higher energy, effectiveness, light weight and good water resistance. The products from polyethylene are become famous in over the decade. However, it has been a target of much criticism due to its lack of degradability [1] especially the plastic bag, agriculture bag product and so on. So during the past two decades the quantity of plastic material used in the in packing application has increased annually at a phenomenal rate. At the present time something like 1000 square miles of polyethylene film are produced in the United Kingdom alone each year. Even if a large percentage of the population can be persuade to take care against creating litter and even if litter collection systems are reasonably efficient, a quantity of unsightly rubbish is bound to accumulate [2]. According to Guillet [3] the most effective way to deal with this litter problem is to reduce the “life time” of the littered objects. The meaning of ‘life time’ is to reduce for their chain ability of the polyethylene material to make it easier to decompose.

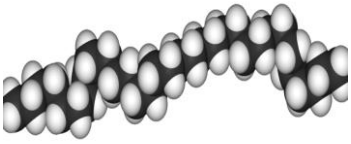

Figure 1.1: Space-filling model of a polyethylene

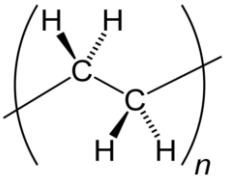

Figure 1.2: The repeating unit of chain showing its stereochemistry

The need to control the proliferation of plastic litter has been recognized for many years and has become increasingly pressing during the last few decades with the discovery by environmental scientists that discarded packaging is responsible for the death of a large number of mammals by ingestion and strangulation [4]. Polyethylene is relatively inert due to its hydrophobic chain and high molecular weight. It has been estimated that polyethylene biodegrades less than 0.5% in 100 years and about 1% if pre-exposed to sunlight for 2 years [5]. LDPE is extensively used for a variety of different applications, resulting in its increased production. Subsequently, the plastic fraction of the municipal solid waste stream has also increased leading to associated urban plastic litter problem. The hazardousness of polyethylene as a waste is associated with its excellent outdoor durability and its inherent resistance to hydrolysis and biodegradation in the environment.

Figure 1.3 Product from polyethylene

1.1.2 Degradability process

Degradability offers a complimentary strategy to deal with this litter problem. One of the simplest ways of modifying the existing polymer is to accelerate the rate of photo-degradation and thermal degradation process already taking place with using the additive such as transition metal corboxylates are particularly suitable for this purpose. Degradability also offers a complimentary strategy to deal with this litter problem. One of the simplest ways of modifying the existing polymer is to accelerate the rate of thermal/photodegradation process already taking place with using the additive such as transition metal corboxylates are particularly suitable for this purpose. Different approaches to develop thermal/photodegradable polyolefins have been adopted, including both copolymerization with ketone or CO groups and addition of thermal/photo initiating metal complexes [6]. Thermal/Prodegradant additives are used to enhance such oxo-biodegradation of polyolefins [7], [8], [9], [10], [11], [12], [13], and [14] and the additives preparation based on cobalt [15], [16], [17], [18] and [19] iron [20], [21], and [22], manganese [23] and [24] and cerium [25] have been commercialized. In addition, the formation of carbonyl groups on the surface increases its hydrophilicity. Consequently, the possibility of further degradation induces a significant enhancement towards mineralization of plastic material [26] and also leads to an increase in the surface area through embrittlement

1.1.3 Thermal Degradation

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to

occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight and molecular weight distribution of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties [27].

1.1.4 Transition metal and carboxylic acid

Transition metal [28] and carboxylic acid containing polymers [29] individually have been reported to act as effective photo/thermal degradation initiators for polyethylene, although the mode of action of all the three is different. Transition metals especially Mn, Fe, Co possess a remarkable ability to decompose the hydroperoxides formed during the oxidation process of polymers. The prooxidant activity of carboxylate acid polymers like EAA can be attributed to ease of hydrogen abstraction from the acidic groups by peroxy radicals. [29]. Combination of all the two components i.e. metal and carboxylate acid based functionality would therefore be expected to show a strong thermal/photo initiating activity.

1.1.5 Cobalt Carboxylate

Cobalt stearate, cobalt palmitate and cobalt laurate are apart of carboxylates group and is also recognize as cobalt salt of stearic acid, palmitic acid and lauric acid. Transition metals like Co, Mn, Fe especially in the form of carboxylates, have been employed to initiate degradation in polyethylene films. The role of these metals/metallic compounds on the photo-degradation of polyethylene has been extensively studied by several authors [28]. However the effect of cobalt stearate, cobalt palmitate and cobalt laurate on the rates of thermal degradation of HDPE polyethylene has not been studied systematically. Although, cobalt stearate is the major additive in cobalt carboxylates group but another cobalt carboxylate additive

like cobalt palmitate and cobalt laurate are used to make the comparison with cobalt stearate efficiency.

In this study, HDPE is used as the raw materials due to the significant disposal problem. Although it caused by major in bag plastic but the rest of litter it's contributes by product from HDPE material and become the pollution of the environment. The present of high temperature of light in HDPE polyethylene with a suitable additive are considered a real alternative to degrade or reduce molecule compound in HDPE polyethylene especially at their backbone.

So, in this thesis will give a systematic study on the effects induced by cobalt carboxylate, especially due to rate on the thermal degradation of HDPE.

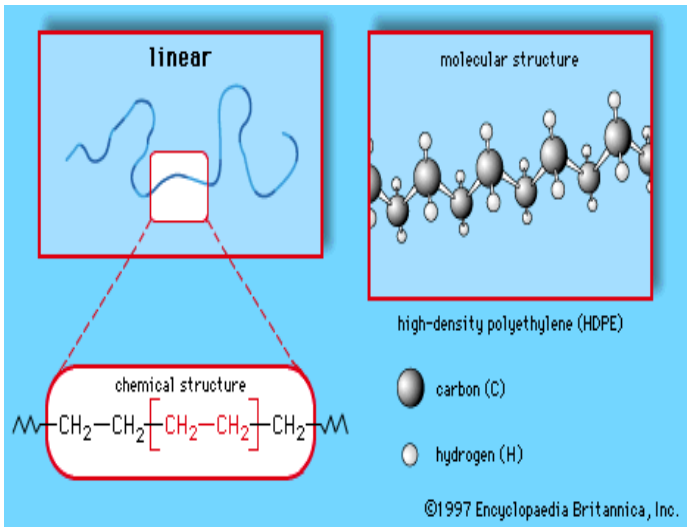

Figure 1.4: Structure of HDPE

1.2 Problem Statement

Nowadays all of component, furniture and also the packaging made from polyethylene as their main substance. For example, the wide application of plastics in agriculture has decisive influence on cultivation practices. Plastic films used as a growing aid in the form of mulch and tunnel covers have increased yield. The litter of this film left behind after the harvest poses serious disposal problem. Effect of the litter accumulation is become an environmental issues. If the problem is not preventing as soon as possible, the issues might become worst. For example, the most product of polyethylene used is plastic bag. Plastic bags are popular with consumers and retailers as they are a functional, lightweight, strong, cheap, and hygienic way to transport food and other products. Approximately 6.9 billion plastic bags are consumed annually in Australia:

- 6 billion of these are high density polyethylene (HDPE), such as supermarket singlet bags or supermarket checkout bags.
- 0.9 billion are low density polyethylene (LDPE), such as boutique bags.
- 67% of HDPE & 25% of LDPE bags are imported with the remainder locally produced.

Below is the two major environmental problem cause from our use of plastic bag [30]:

Firstly, plastic bags are one of the most damaging forms of litter.

- At least 80 million plastic bags end up as litter on our beaches, streets and parks each year
- While they are estimated to only be 2% of the litter stream, they have a significant environmental impact because they can take up to 1,000 years to break down.
- Their persistence in the environment means that they can entangle and harm marine life and other animals. In fact, the World Wide Fund for Nature estimates that more than 100,000 whales, seals, turtles, and birds die every year as a result of plastic bags.

- For example, on 24 August 2000, a Bryde's whale died in Trinity Bay, 2 km from central Cairns. An autopsy found that the whale's stomach was tightly packed with plastic, including supermarket bags, food packages, bait bags, three large sheets of plastic, and fragments of garbage bags. There was no food in its stomach. When the dead animal decays, the plastic bags are freed to be re-ingested by other animals in years to come.
- On land, plastic bag litter can block drains and trap birds. They also kill livestock. One farmer near Mudgee NSW carried out an autopsy on a dead calf and found 8 plastic bags in its stomach. The loss of this calf cost the farmer around $500.
- Cleaning up this litter is expensive. Australian local and state governments spend over $200 million a year picking up litter (all forms).

Secondly, the plastic shopping bag, a single use item, is a symbol of a wasteful society: [31]

- 20 million Australians used 6.7 billion plastic checkout bags this year (down from 6.9 billion the previous year). That's nearly 1 plastic bag per person per day or 345 bags per person per year.
- A person's use of a plastic checkout bag can be counted in minutes - however long it takes to get from the shops to their homes.
- The amount of petroleum used to make one plastic bag would drive a car about 115 metres. The 6.9 billion plastic checkout bags we use every year is enough to drive a car 800 million kilometres or nearly 20,000 times around the world - i.e. 4 round trips to the Sun.
- Less than 3% of Australia's plastic bags are currently being recycled, despite recycling facilities being available at major supermarkets.
- Only an estimated 19% of the 3.7 billion plastic supermarket shopping bags handed out in Australia every year, are being reused by households as kitchen bin liners.
- In many council areas, plastic bags are the single main contaminant of curbside recycling.

- Plastic bags are not free to consumers - they are actually adding an estimated $173 million a year to Australia's grocery bills.

The controlled photo degradation of plastic (polyethylene) afford a workable solution not only to this problem but open new possibilities of the new programmed removal of the film even during the growing period of time within the crops when this is desirable.

Solid waste disposal and litter like polyethylene are among the many problems that arise from the relationship between man or women and his or her environment whereby the litter is related with human inventor. The present generation commodity plastics, especially the packaging materials, contribute significantly to resolve the solid waste disposal problem. The use of plastic materials that can re-enter the biological life cycle, appear to be one of the most promising solution to this problem after the first photodegradation process is done. One of the most common techniques to decrease the lifetime of polyethylene with used to render a polyolefin degradable is to add prooxidants at the processing stage. The additives normally used for the initiation of degradation process are organosoluble transition metal ions, aromatic ketones, dithiocarbamates, acetyl acetonates, which act as thermal and/or photo-oxidant for the polymer also can effectively enhance the degradability of that material.

1.3 Objective and Scope

The objective of this research is to decrease the litter problem cause of polyethylene (HDPE) product and prevent it with use cobalt carboxylate as additives, also to determine the effective concentration of additive adding into HDPE to thermal degradation initiator with the scope of this research are:-

i. To investigate the characteristic of cobalt carboxylates.
ii. To investigate the thermal treatment effect before and after adding cobalt carboxylate additive into HDPE film including duration of thermal treatment exposed.
iii. To investigate the effect of increasing cobalt carboxylate's concentration in accelerating thermal degradation of polyethylene.
iv. To develop the effective additive preparation to increase the thermal degradtion process.

1.4 Research Contribution

This research can help in minimizing the environmental impact and aid by accelerate of thermal degradation of polyethylene when exposed to the heat at specific temperature. Whereas the decrease service life of typical plastic is strongly influence by the thermal degradation caused by high heating. So the additives such as cobalt carboxylate can be used to control the thermal stability and acceleration of thermal degradation process to make of polyethylene product easily to decompose.

1.5 Thesis Layout

This thesis has 5 chapters. Chapter 1 introduces a background of the study and also about the litter from polyethylene where become an environment issues and the way to solve that problem. It is also includes objective, scope and problem statement. Chapter 2 is about literature review which includes topic extensively researched of polyethylene; enhance a degradability process with use aid additive and variety of sources is cited. Literature research contains information relevant and directly related to research in this study. In Chapter 3, the methodology develops the steps needed to study about effect of cobalt carboxylate in strength of polyethylene will be discussed. Chapter 4 will be discussing about the results obtained from the experiment. It includes the efficiency concentration of used the cobalt carboxylate as

the additive. Lastly Chapter 5 will conclude the thesis and provide recommendations on how to improve the way to make polyethylene especially High Density Polyethylene (HDPE) easier to decomposed and decrease the litter problem cause of polyethylene to importance of environmental issues.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nowadays, the quantity of plastics material used in packaging application, furniture, and addition accessories of women has increased annually at a phenomenal rate. The quality is important but the more importance is to develop the effective additive to accelerate the photo degradation process and solve the litter problem from polyethylene which is decomposed it easily. Many of scientists doing their research to solve this problem and several of the research have been take as an initiative in the process to accelerate the degradability and resolve that problem.

2.2 Use High Density Polyethylene (HDPE) as Raw Material

The plastic industry plays a major role in the economy of the United States. The world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century close to 1.5 million tons per year in 2000 [32]. Total resin consumption in Malaysia increased by 8% from 1.6 million MT in 2004 to 1.72 million MT in 2005, of which about 65% were polyolefins (PE and PP). Plastics production systematically increases, thus also plastics waste amount grows [33] .In the year 2000 and above, direct jobs in plastics accounted for 1.5 million employees while support/supply jobs added about 0.9 million. The total 2.4 million jobs accounted for more than 2 percent of the total workforce in the United States.

Between 1973 and 2000 above, the production of plastics in the United States grew at an average annual rate of 4.7 percent [34]. The total production included a number of various plastics. From the previous research about the production volume in 2000 for the major plastic, there increase to the year which accounted for 78 percent of the annual production:

Polypropylene (PP)	7,154
Polyvinyl chloride (PVC)	6,565
High Density Polyethylene (HDPE)	6,349
Low Density Polyethylene (LDPE)	3,443
Linear Low Density Polyethylene (LLDPE)	3,614
Polyester, thermoplastic (PETE)	3,195
Polystyrene (PS)	3,111
Phenolic	1,979
Total	35,410

Units: 1,000 metric tons

Table 2.1: U.S Production of Plastic

Acrylonitrile-butadiene-styrene	(ABS)
663	
Epoxy	
315	
Nylon	582
Phenolic	1,979
Polyester, thermoplastic	3.195
High Density Polyethylene	6,349
Low Density Polyethylene	3,443
Linear Low Density Polyethylene	3,614
Polypropylene	7,154
Polystyrene	3,111
Polyvinyl chloride	6,565
Styrene acrylonitrile	58

Urea and melamine	1,440
Others	7,010
Total	45,479
Units: 1,000 metric tons	

Based on the table above, the best raw material to choose in this research is polyethylene especially High Density Polyethylene type. HDPE Polyethylene also a famous base material to produce a bottle, plastic bag, furniture, toys and all the things in this decade we use a lot of bottle and plastic bag in our life and related to litter problem and environmental issues.

2.3 Characteristic of HDPE and LDPE Polyethylene

Polyethylene density is a characteristic used to distinguish between grades of polyethylene plastics that are expressed as g/cm^3. This measurement varies among petroleum-derived plastics due to differences in crystallization structure formed during the polymerization of ethene. In addition, density is affected by molecular weight of the final product. Branching, or the bonding of ethene monomers to hydrogen molecules to form polymers, also determines density. In fact, this last factor is the primary difference between high-density polyethylene (HDPE) and low-density polyethylene (LDPE).

Most people are familiar with HDPE and LDPE plastics. However, there are numerous other grades of polyethylene density. That's because different types of polyethylene are obtained according to the methods employed to induce polymerization. For instance, material produced by the addition of a free-radical initiator (radical polymerization) often produces a different polyethylene density than one made by the use of a catalyst, such as chromium and/or silica. In addition, each type offers specific advantages.